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Structure and Thermochemistry of Perrhenate Sodalite and Mixed Guest Perrhenate/Pertechnetate Sodalite

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ABSTRACT: Treatment and immobilization of technetium-99 (^{99}Tc) contained in reprocessed nuclear waste and present in contaminated subsurface systems represents a major environmental challenge. One potential approach to managing this highly mobile and long-lived radionuclide is immobilization into micro- and mesoporous crystalline solids, specifically sodalite. We synthesized and characterized the structure of perrhenate sodalite, $Na_8[AlSiO_4]_6(ReO_4)_2$, and the structure of a mixed guest perrhenate/pertechnetate sodalite, $Na_8[AlSiO_4]_6(ReO_4)_{2-x}(TcO_4)_x$. Perrhenate was used as a chemical analogue for pertechnetate. Bulk analyses of each solid confirm a cubic sodalite-type structure ($P\bar{4}3n$, No. 218 space group) with rhenium and technetium in the 7+ oxidation state. High-resolution nanometer scale characterization measurements provide first-of-a-kind evidence that the ReO_4^- anions are distributed in a periodic array in the sample, nanoscale clustering is not observed, and the ReO_4^- anion occupies the center of the sodalite β-cage in $Na_8[AlSiO_4]_6(ReO_4)_2$. We also demonstrate, for the first time, that the TcO_4^- anion can be incorporated into the sodalite structure. Lastly, thermochemistry measurements for the perrhenate sodalite were used to estimate the thermochemistry of pertechnetate sodalite based on a relationship between ionic potential and the enthalpy and Gibbs free energy of formation for previously measured oxyanion-bearing feldspathoid phases. These results suggest that micro- and mesoporous crystalline solids maybe viable candidates for the treatment and immobilization of ^{99}Tc.

INTRODUCTION

Development of a sustainable nuclear fuel cycle, which must include closing the back-end by recycling and/or disposing of used nuclear fuel, is a key component of the nuclear energy renaissance (12% of the electrical energy worldwide[1] and 19% in the United States[2]). Disposition of radioactive waste generated by the nuclear fuel cycle and nuclear weapons production during

the Cold War era is one of the most pressing environmental challenges facing the United States and the international community.[3-4] Furthermore, proposed waste management strategies are complicated by the inventory of long-lived radionuclides, such as technetium (^{99}Tc), and the time-scales considered for disposal.

Since its discovery in 1937 by Perrier and Segre,[5-6] the global inventory of ^{99}Tc has increased steadily. Technetium-99 (β = 293.7 keV, $t_{1/2} = 2.1 \times 10^5$ years), a byproduct of ^{235}U and ^{239}Pu fission, comprises a significant component of radioactive waste due to its high fission yield—~5%. The world-wide inventory of ^{99}Tc requiring disposition is estimated to have quadrupled to ~305 MT from 1994 to 2010 because of nuclear energy production[7] Additionally, US weapons production sites must dispose of ~5.1 MT of ^{99}Tc (~3.5 MT at the Savannah River Site and ~1.6 MT at the Hanford Site).[8] Treatment and immobilization of ^{99}Tc contained in reprocessed nuclear waste presents a major challenge because ^{99}Tc volatilizes at the temperatures (~1100 ºC) required for vitrification, the preferred international treatment method.[8-11] The immobilized nuclear waste glass is destined for long-term storage in a geologic repository.

The chemistry of ^{99}Tc suggests that under aerobic environmental conditions, the stable heptavalent Tc 7+ pertechnetate anion ($^{99}TcO_4^-$) is dominant. This oxyanion is soluble and readily migrates through the environment because it does not adsorb well onto mineral surfaces, soils, or sediments. Because of the long half-life, abundance, and high environmental mobility of ^{99}Tc, incorporating it into durable matrices other than glass is an attractive waste management strategy.[12] For example, recent studies have examined the possibility of incorporating ^{99}Tc in the 4+ oxidation state into the structure of iron-based minerals.[13-19] Although various countries are pursuing vitrification as the primary waste management strategy for other radionuclides (e.g., ^{137}Cs, ^{90}Sr, U-isotopes, etc.), one approach that has been considered previously but not pursued

for disposition and remediation of TcO_4^- is encapsulating the radionuclide into micro- and mesoporous crystalline solids, such as the feldsphathoid phase sodalite.

Micro- and mesoporous solids represent a family of >150 crystalline phases, which support a variety of industrial processes (petrochemical cracking, ion exchange for water softening and purification, and gas separation). These porous materials contribute an estimated $350 billion to the global economy as part of the world's chemical industry. The material's structure consists of a three-dimensional (3D) framework composed of alternative TO_4 (T = Al or Si) tetrahedral units covalently joined via oxygen atoms. The 3D framework structure contains a pore or cavity system that can expand (microporous = 2.5 to 20 Å; mesoporous = 20 to 500 Å) to enclathrate various guest anions and organic molecules by cooperative changes in the T-O-T bond angle. For example, aluminosilicate sodalites, both natural and synthetic, can vary widely in composition but have the general formula of $M_8(Al_6Si_6O_{24})X_2$, where M is a monovalent cation (such as Cs^+, K^+, Na^+, etc.) and X can vary between monovalent or divalent anions (such as OH^-, Cl^-, Br^-, I^-, MnO_4^{2-}, ReO_4^-, or theoretically TcO_4^-).[20-31]

Here we use Re as a nonradioactive analogue for ^{99}Tc, because under oxidizing conditions both elements are oxyanions and they have similar metal oxygen bond lengths (Tc–O = 1.702 Å; Re–O = 1.719 Å) and ionic radii (TcO_4^- = 2.52 Å; ReO_4^- = 2.60 Å).[7,32-34] However, under reducing conditions it is easier to reduce Tc in comparison to Re from 7+ to 4+ because of the difference in standard reduction potential of ReO_4^-/ReO_2 = 0.510 V versus TcO_4^-/TcO_2 = 0.738 V.[8,35-36] Thus, the use of Re as a nonradioactive analogue for ^{99}Tc is only applicable under oxidizing conditions where both species are expected to remain in the 7+ oxidation state.

Studies by Dickson et al. [37-39] suggest that the ReO_4^- anion—and by analogy the TcO_4^- anion—is incorporated into the sodalite β-cage and that anion selectivity for the sodalite β-cage is size-

dependent. However, the afore-mentioned studies mainly used changes to the chemical composition and bulk x-ray powder diffraction spectra to support their conclusions. Although these results provide key insights on the factors that influence ReO_4^- incorporation in to the sodalite β-cage, they do not provide definitive evidence regarding location of the ReO_4^- anion in the crystalline matrix. As a result, the question of the location and distribution of the ReO_4^- anion remains unanswered. Additionally, the key question of whether or not the TcO_4^- anion can be incorporated into the sodalite structure also remains elusive.

In this study, we synthesized and characterized the structure of perrhenate sodalite using, for the first time, a combination of time-of-flight (TOF) neutron powder diffraction (NPD) and aberration-corrected high annular angular dark field (HAADF) scanning transmission electron microscopy (STEM). The TOF-NPD was used to more precisely determine the oxygen positions and refine structural parameters and the aberration-corrected HAADF STEM was used to determine the location and distribution of the ReO_4^- anion in perrhenate sodalite. Additionally, we synthesized and characterized the oxidation state of Re and ^{99}Tc in a mixed guest perrhenate/pertechnetate sodalite using x-ray absorption spectroscopy, extended x-ray absorption fine structure, and x-ray powder diffraction. Lastly, calorimetric measurements for the perrhenate sodalite were used to estimate the thermochemistry of pertechnetate sodalite based on a relationship between ionic potential and the enthalpy and Gibbs free energy of formation for previously measured oxyanion-bearing feldspathoid phases.

EXPERIMENTAL

Synthesis of Perrhenate Sodalite and Mixed Guest Perrhenate / Pertechnetate Sodalite. Perrhenate sodalite was synthesized using hydrothermal methods by treating Zeolite 4A with 8M NaOH in the presence of excess sodium perrhenate at 225°C and 400 psi in an autoclave for 7 d

(168 h). The mixed guest perrhenate/pertechnetate sodalite was also prepared hydrothermally using a similar synthesis approach as above with a 11:1 mole ratio of $NaReO_4$ (0.021 moles) to $NaTcO_4$ (0.0019 moles). For additional details on the synthesis see the Supporting Information section.

X-ray Diffraction. The powder XRD spectrum of the homogenized perrhenate sodalite sample was measured with a Panalytical X'Pert PRO diffractometer using CuK_α radiation (λ = 1.54060 Å). Data were collected in 0.017° steps over the 2θ range 5–110°. The powder XRD spectrum for the mixed guest perrhenate/pertechnetate sodalite sample was measured with a Bruker D8 Advance x-ray diffractometer using CuK_α radiation (λ = 1.54060 Å). The samples were ground in an agate mortar and pestle, mixed with a 1:10 collodion/amyl acetate mixture, and smeared onto a square glass slide. The XRD data were collected in 0.02° step size and a dwell time of 1 s over the 2θ range 5–70°.

X-ray Absorption Spectroscopy. Rhenium x-ray absorption fine structure (XAFS) analysis was conducted by placing approximately 200 mg of sample in a Teflon holder sealed with Kapton tape. The bulk Re L_{II}-edge (11,959 eV) X-ray Absorption Near Edge Structure (XANES) spectrum of the perrhenate sodalite was collected in transmission at Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-2. The beamline configuration consisted of a cryogenically cooled Si(220), ϕ = 90°, double-crystal monochromator with the second crystal detuned by 70% to reduce the harmonic content of the beam. Incident and transmitted beam intensity was determined using nitrogen-filled ion chambers. Data were normalized and corrected for self-absorption using Athena.[40]

Technetium XAFS analysis was conducted by mixing 100 mg of mixed Re/Tc sodalite with 100 mg of chloride sodalite and adding the 200 mg mixture to a Teflon holder sealed with

Kapton tape. The bulk Tc K-edge (21,047) XANES spectrum of the mixed guest perrhenate/pertechnetate sodalite was collected in fluorescence at the National Synchrotron Light Source on beamline X27A with a HPGe detector. Data were averaged using Athena and are not corrected for detector dead time or self-absorption because neither effect was significant at the detector count rates and pertechnetate concentrations used in this study (1 mol % pertechnetate in the mixed guest perrhenate/pertechnetate sodalite).

For additional details on the XAS spectrum fitting see Supporting Information.

Neutron Powder Diffraction. Time-of-flight powder neutron diffraction (PND) data were collected using 1.312 gram samples of sodium perrhenate [$Na_8(AlSiO_4)_6(ReO_4)_2$] contained in an 8 mm diameter vanadium sample can at 298 K. The PND patterns were collected using the POWGEN (BL-11A) neutron powder diffractometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory, Oak Ridge, TN. Diffraction profiles were collected using center wavelengths 1.066 Å and 2.665 Å, providing a d-spacing range from 0.57 to 6.18 Å. Rietveld refinements of the data were performed using the GSAS software package along with the EXPGUI interface.[41-42] The bound coherent scattering lengths 3.62 ± 0.02 fermi (fm) for sodium, 3.449 ± 0.005 fm for aluminum, 4.149 ± 0.001 fm for silicon, 9.2 ± 0.2 fm for rhenium, and 5.803 ± 0.004 fm for oxygen. The large bound coherent scattering length of oxygen allows the oxygen positions to be determined using neutron diffraction with more accuracy than with XRD. Additionally, the difference in the bound scattering length for the aluminum, rhenium, and silicon atoms allows these elements to be distinguished better using neutron powder diffraction than with XRD. The atomic structure for $Na_8(AlSiO_4)_6(ReO_4)_2$ previously reported was used as the starting model for calculating the diffraction patterns.[29-30]

Microscopy imaging. Atomic resolution aberration-corrected STEM images were obtained with a Nion Ultra STEM 60-100 electron microscope. This was equipped with a cold field emission gun and operated at 100kV with a 3rd generation C3/C5 aberration corrector. The aberration-corrected HAADF STEM images were performed with a probe current of 80 pA. Beam damage was readily apparent when imaging in the STEM (see Fig. SI2) and electron dose was minimized by using fast scan speeds at the largest field of view that atomic columns could still be resolved. Perrhenate sodalite powder was suspended in 50 mL of IPA and a 10 μL droplet was cast onto a 3mm copper lacey carbon TEM grid and the solution was allowed to evaporate. The drop cast TEM grid was then prebaked in a vacuum oven station at 160°C for 8 hours in a vacuum at ~10^{-6} torr and then allowed to cool under vacuum for 10 hours. STEM imaging was performed on a single grain of perrhenate sodalite that was positioned on the lacey carbon in a crystallographic orientation close to [111] zone axis. STEM stage tilts were then used to properly orient the sample into a [111] zone axis for atomic column resolution imaging. The [111] zone axis was selected because it was ideal for observing the ReO_4^- anion present inside the sodalite β-cage. Details of the scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements for both the perrhenate sodalite and mixed perrhenate/pertechnetate sodalite are provided in the Supporting Information.

Calorimetry. High temperature oxide melt solution calorimetry was performed using a Tian Calvet twin calorimeter described in detail by Navrotsky.[43-44] In the drop solution calorimetry experiment, samples in the form of pellets (between 4 and 6 mg) were dropped from room temperature (298 K) into the molten $2PbO{\cdot}B_2O_3$ at the calorimeter temperature in a platinum crucible. Air was flushed over the solvent at 90 ml/min. The calorimeters were calibrated using the heat content of 5 mg α–Al_2O_3 pellets.

A preliminary furnace test was performed before conducting the calorimetry measurements to verify the complete dissolution of the sample. Pellets of approximately 5 mg were prepared and dropped in molten lead borate solvent ($2PbO•B_2O_3$), maintained at 973 K in a furnace. The dissolution process started immediately and finished in a minute. After quenching the melt, no undissolved material was found.

RESULTS AND DISCUSSION

Synthesis and Characterization of Perrhenate Sodalite. The hydrothermal reaction produced a crystalline powder with perrhenate sodalite particles that ranged from 0.5 to 5 μm for individual crystals (Fig. SI1) and agglomerated crystals 10 μm or less. The chemical composition was within the experimental error of what is expected for a stoichiometric sample (see Table S1).

To confirm the bulk rhenium oxidation state following hydrothermal synthesis, X-ray absorption near-edge spectroscopy (XANES) was performed on the resulting solid. The Re L_2-edge XANES spectra of the four standards are shown in Fig. SI3.[35] Two major changes are observed in the rhenium standard reference spectra as one proceeds from Re metal (Re [0] oxidation state) to ReO_4^- (Re [7+] oxidation state). First, the absorption edge shifts to higher energy because the binding energy of the electron increases as the formal oxidation state increases; there are fewer electrons to screen the charge of the nucleus from the 2p electrons. Second, the area of the large peak at the absorption edge—the "white line," which is associated with the 2p to 5d transition—increases as the rhenium oxidation state increases because the area is proportional to the number of vacancies in the 5d orbitals (Fig. SI3). Analysis of the perrhenate sodalite XANES spectrum indicates that only ReO_4^- is present (Fig. SI3) but the fit using the standard reference spectrum suggests that $KReO_4$ is less than optimal (Table SI2). The

discrepancy is due to the difference between the local environments of ReO_4^- in perrhenate sodalite and $KReO_4$, as discussed below.

In addition to these major differences, the XANES region just above the edge contains features due to extended x-ray absorption fine structure (EXAFS), especially those caused by multiple scattering. The major changes are clearly seen in Fig. SI3 as the spectrum from standard compounds transition through the range of oxidation states from the 4+ (ReO_2) to 7+ ($KReO_4$). The smaller EXAFS contributions may be seen in the size and spacing of the features at energies above that of the white line. As noted above, the EXAFS contributions result in slightly different spectra for $KReO_4$ versus perrhenate sodalite. Although both materials contain the tetrahedral coordinated ReO_4^- anion, in the $KReO_4$, the potassium ion interacts strongly with the ReO_4^- anion (the only anion present in ReO_4^-); in perrhenate sodalite, the sodium ions interact with both the negatively charged sodalite framework and the ReO_4^- anion. The resulting weakening of the interaction between ReO_4^- and the sodium ions is reflected in the decrease of the Re–O bond distance in perrhenate sodalite, 1.729(7) Å, versus $NaReO_4$, 1.728(2) Å,[45] and in $KReO_4$, 1.723(4) Å[46-47] (Fig. 1 and Table SI3). The observed shortening of the Re–O bond length in the sodalite crystal structure is consistent with the shortening of the Mn–O bond length in permanganate sodalite.[31,48]

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Fig. 1. Extended Re L_2-edge EXAFS spectrum of perrhenate sodalite, $Na_8[AlSiO_4]_6(ReO_4)_2$. The EXAFS data and fit are depicted as a solid gray line and black circles, respectively. Fit range: $2 < k < 11$ (a); $0.8 < R < 2.0$ (b); the number of independent points was 8.6, and the number of parameters was 4.

A combination of powder x-ray diffraction (pXRD) (not shown) and neutron powder diffraction (NPD) (Fig. 2) measurements were performed on the perrhenate sodalite sample. The crystallography data are provided in Table 1. The refined atomic positions, site occupancies, and atomic displacement parameters are given in Table SI4 for the NPD results. It was possible to refine the anisotropic displacement parameters for all of the atoms with the exception of aluminum with the NPD results (see Table SI5). For the aluminum atom, the atomic displacement parameter was ~5 times smaller than the silicon atom; one explanation for this difference is that portion of the aluminum sites have been replaced by silicon atoms, which has a smaller neutron cross-section. The data was subsequently refined with the aluminum site occupied by both aluminum and silicon atoms, which resulted in site occupancies of 83(7)% aluminum and 17(7)% silicon. The refined value of U_{iso} only slightly increased to 0.47(9) × 100, and the χ^2 decreased slightly to 2.109. The formula obtained by refining the site occupancy of the oxygen atom, labeled as O2 in Table SI4 – SI6, is $Na_8(AlSiO_4)_6(ReO_{3.75})_2$, compared with $Na_8(Al_{0.83}Si_{1.17}O_4)_6(ReO_{3.75})_2$ when the aluminum site is shared by both aluminum and silicon. Similar to the NPD, the pXRD results indicate a sodalite-type structure with a $P\bar{4}3n$ (No. 218) space group and lattice parameter a = 9.15283(8) Å (Table SI6). These bulk measurements are consistent with the results obtained previously by Mattigod and colleagues.[29-30]

Fig. 2. Rietveld refinement profiles of powder neutron diffraction data for perrhenate sodalite, $Na_8[AlSiO_4]_6(ReO_4)_2$. The neutron diffraction data were collected using two different center wavelengths to access different d-spacing ranges (d-spacing from 0.5 to 3.0Å on [a] and d-spacing from 1.1 to 6.2Å [b]).

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